

VIA-FILLING MATERIAL AND PROCESS FOR FABRICATING  
SEMICONDUCTOR INTEGRATED CIRCUIT USING THE SAME

FIELD OF THE INVENTION

The present invention relates to a via-filling material filled in the via hole when fabricating a multi-layered wiring structure in accordance with the dual damascene process and a process for  
5 fabricating a semiconductor integrated circuit using the via-filling material.

BACKGROUND OF THE INVENTION

Conventionally, polysilicon or aluminum has been widely  
10 used for forming interconnections in a semiconductor integrated circuit but now there is the need for materials having further reduced resistance, which can replace such polysilicon or aluminum materials in order to accomplish high performance and micropatterns necessary for high-speed data transmission in semiconductor integrated circuits.

15 For this purpose, forming metal lines of the semiconductor integrated circuit by using copper instead of aluminum used in the past has been attempted. However, patterning by dry etching as employed when forming the conventional aluminum connection is difficult with copper and also the corrosion resistance of copper is inferior. So as a  
20 process for fabricating semiconductor integrated circuit comprising metal lines inside and on the surface of the inter-layer film and contacts connecting these metal lines, both of which are made of copper, a process called dual damascene process has now been developed.

In the conventional process of fabricating semiconductor

integrated circuit according to dual damascene technique based on the via-first approach, via holes are first formed through the upper  $\text{SiO}_2$  inter-layer film to the stopper film at the position where metal line is located below. Thereafter, the via holes are filled with a via-filling  
5 material such as an organic film and trenches of a certain width are formed in a depth which does not reach the stopper film.

As the organic film, ARC (Anti Reflective Coating), specifically a composition obtained by adding poly(vinyl phenol) or poly(methyl methacrylate) to a base resin comprising polyimide and novolak is used  
10 (see for example, JP-A-2001-203207).

Also, as the via-filling material filled in the via hole, photoresist materials, melamine derivatives, guanamine derivatives, glycoluril derivatives, urea derivatives and succinyl amide derivatives are used (see for example, JP-A-2000-195955).

15 In the conventional dual damascene process, the organic materials mentioned above are used as the via-filling material filled in the via holes. However, when conducting plasma etching of the upper inter-layer film and the via-filling material in order to form a trench, via-filling material 307 protrudes from upper inter-layer film 302 within  
20 trench 310 as shown in Fig. 3, because the etching rate of the via-filling material is lower than the etching rate of the upper inter-layer film.

Furthermore, when  $\text{C}_4\text{F}_8$  is used as etching gas, fluorocarbon deposition is easily generated from the decomposition in plasma or reaction products. Such deposition often sticks around the protruded  
25 via-filling material and prevents downward plasma etching because the deposition serves as a mask. Accordingly, when the via-filling material in the via hole is removed after completing the simultaneous etching of

the upper inter-layer film and via-filling material, deposition 308 which is chemically stable and hard to decompose remains in the opening part of via hole 306 as shown in Fig. 4.

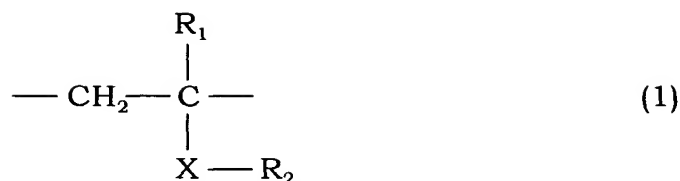
When deposition remains in the opening part of via hole, metal lines in the upper layer cannot be formed well, leading to the problem of disconnection in the fabricated semiconductor integrated circuit.

### SUMMARY OF THE INVENTION

The present invention has been made in order to solve the above problems and the first object of the present invention is to obtain an organic via-filling material which has a higher etching rate than the upper inter-layer film and thus does not protrude from the upper inter-layer film within the formed trench even in the case of etching the via-filling body obtained by filling and solidifying the via-filling material in a via hole and insulating films such as upper inter-layer film in the dual damascene process.

The second object of the present invention is to provide a process for fabricating a semiconductor integrated circuit in which the step of removing deposition is unnecessary because deposition does not remain in the opening part of the via hole, and by which upper metal lines can be formed well without causing disconnection or the like.

The via-filling material of the present invention is used to fill a via hole in the insulating film previously where a trench wider than the via hole is formed by conducting plasma etching, the material comprising a polymer containing a repeat unit represented by the following formula (1):



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wherein R<sub>1</sub> is a member selected from the group consisting of hydrogen atom, fluorine atom, chlorine atom, bromine atom and methyl group; R<sub>2</sub> is a member selected from the group consisting of hydrogen atom, C<sub>1-3</sub> alkyl group and C<sub>1-4</sub> alkyl group in which the hydrogen atom is substituted by at least one kind of atoms of fluorine, chlorine and bromine atom; and X is -C(=O)O- or -S(=O)<sub>2</sub>O-.

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Preferably, the polymer constituting the via-filling material of the present invention has a weight average molecular weight of 1,000 to 200,000.

The via-filling material of the present invention comprises a copolymer of a first monomer and a second monomer, the first monomer being represented by the formula (2):

20



wherein R<sub>1</sub> is a member selected from the group consisting of hydrogen atom, fluorine atom, chlorine atom, bromine atom and methyl group; R<sub>2</sub> is a member selected from the group consisting of hydrogen atom, C<sub>1-3</sub> alkyl group and C<sub>1-4</sub> alkyl group in which the hydrogen atom is substituted by at least one kind of atoms of fluorine, chlorine and

25

bromine atoms; and X is  $-\text{C}(=\text{O})\text{O}-$  or  $-\text{S}(=\text{O})_2\text{O}-$ ; and the second monomer contains an unsaturated group which brings about a copolymerization reaction with the first monomer and a functional group capable of crosslinking the prepared copolymer.

5           The first process for fabricating a semiconductor integrated circuit of the present invention comprises the steps of: forming a stopper film on the surface of a lower insulating film on which a first conductor is formed and laminating an upper insulating film on the stopper film; forming a via hole leading from the surface of the upper insulating film to  
10 the surface of the stopper film at the position where the first conductor is located below; applying any of the via-filling materials of the present invention on the surface of the upper insulating film to fill the via hole with the via-filling material; forming a resist pattern defining an opening part including the via hole on the applied film made of a via-filling body  
15 obtained by solidifying the via-filling material; forming a trench of a depth which does not reach the stopper film in the upper insulating film by dry etching the upper insulating film and the via-filling body using the resist pattern as a mask; removing the resist pattern, the applied film made of via-filling body and the via-filling body remaining in the via  
20 hole and etching the stopper film appeared on the bottom of the via hole, thereby exposing the first conductor; and forming a second conductor in the trench and the via hole.

          The second process for fabricating a semiconductor integrated circuit comprises the steps of: forming an insulating film on a  
25 substrate; forming a via hole in the insulating film; applying any of the via-filling materials of the present invention on the surface of the insulating film to fill the via hole with the via-filling material; forming a

resist pattern defining an opening part including the via hole on the applied film made of a via-filling body obtained by solidifying the via-filling material; forming a trench of a depth which does not reach the substrate in the insulating film by dry etching the insulating film and  
5 the via-filling body using the resist pattern as a mask; removing the resist pattern, applied film made of via-filling body and the via-filling body remaining in the via hole; and forming a conductor in the trench and the via hole.

#### 10                    BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a cross-sectional view illustrating the steps of fabricating a semiconductor integrated circuit of Embodiment 1 using the via-filling material according to a via-first dual damascene process.

15                    Fig. 2 is a cross-sectional view illustrating the steps of fabricating a semiconductor integrated circuit of Embodiment 2 using the via-filling material according to a via-first dual damascene process.

Fig. 3 is a cross-sectional view illustrating a protrusion of the via-filling body.

20                    Fig. 4 is a cross-sectional view illustrating deposition around a via hole.

#### DETAILED DESCRIPTION

##### EMBODIMENT 1

25                    Fig. 1 is a cross-sectional view illustrating the steps of fabricating a semiconductor integrated circuit of Embodiment 1 using the via-filling material of the present invention, according to the via-first

dual damascene process.

Referring to Fig. 1, lower insulating film 104 is formed on semiconductor substrate 100 and lower metal line 105 which is the first conductor is buried in this lower insulating film 104. Then upper  
5 insulating film 102 is laminated on the surface of lower insulating film 104 and metal line 105, interposing etching stopper film 103 therebetween (Fig. 1 (a)).

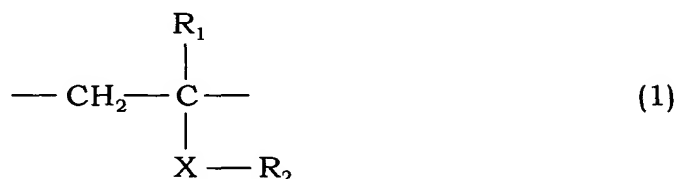
In this embodiment, SiOC is used for lower insulating film 104 and upper insulating film 102 while silicone oxide insulating  
10 materials such as  $\text{SiO}_2$  and SiOF or organic spin-on-glass insulating materials such as SilK (available from Dow-Chemical Co. Ltd.) can also be used. On the other hand, silicone nitride films such as SiN and SiON are used for etching stopper film 103.

As the next step, according to a usual photolithographic  
15 method, resist pattern 101 having a hole at the position where lower metal line 105 is located below is formed by using a commercially available photosensitive photoresist on upper insulating film 102 (Fig. 1 (b)). The formation of resist pattern 101 here is not particularly limited and the type of resist and photolithographic technique are selected  
20 depending on the resist dimensions required. For example, novolak-naphthoquinone i-ray resist materials or chemically amplified resist materials sensitized within a wavelength of KrF excimer, ArF excimer and  $\text{F}_2$  excimer can be used. EB (electron beam) resist materials and X-ray resist materials can also be used.

25 Next, via hole 106 is created in upper insulating film 102 by dry etching upper insulating film 102 (Fig. 1 (c)) and resist pattern 101 is removed by peeling (Fig. 1 (d)). Dry etching is conducted by using a gas

containing a fluorine gas such as CHF<sub>3</sub> or C<sub>4</sub>F<sub>8</sub> as a main component but as another etching gas, a mixed gas of HF<sub>3</sub>/CF<sub>4</sub>/O/Ar can also be used. To remove resist pattern 101, O<sub>2</sub> ashing and cleaning with organic amine are conducted.

5                    Thereafter, via hole 106 is filled with via-filling material 117. More specifically, via hole 106 is filled with via-filling material 117 and leveled (Fig. 1 (e)) by dropping and spin-coating on semiconductor substrate 100 which has an insulating film with via hole 106, a solution obtained by dissolving in an organic solvent a polymer containing a  
10    repeat unit represented by the formula (1):



15                    (wherein R<sub>1</sub> is a member selected from the group consisting of hydrogen atom, fluorine atom, chlorine atom, bromine atom and methyl group; R<sub>2</sub> is a member selected from the group consisting of hydrogen atom, C<sub>1-3</sub> alkyl group and C<sub>1-4</sub> alkyl group in which the hydrogen atom is  
20    substituted by at least one kind of atoms of fluorine, chlorine and bromine atom; and X is -C(=O)O- or -S(=O)<sub>2</sub>O- ).

                    The repeat number “n” of the repeat unit of the polymer is preferably 5 to 1,000. When n is less than 5, film formability decreases while when n is more than 1,000, the viscosity of the polymer solution  
25    increases and the thickness of the via-filling material remaining on insulating film 102 becomes large, necessitating extra steps of removing by polishing or etching back.



The weight average molecular weight of the polymer is preferably 1,000 to 200,000. When the weight average molecular weight is less than 1,000, crack is generated in the via-filling body formed after baking. When the weight average molecular weight is  
5 more than 200,000, the solubility of the polymer in solvents decreases and a solution having a required concentration cannot be obtained.

The concentration of the solution obtained by dissolving the polymer in an organic solvent is preferably 3 to 20 % by weight. When the concentration of the solution is less than 3 % by weight, the via hole  
10 cannot be filled with the via-filling material uniformly. When the concentration of the solution is more than 20 % by weight, the viscosity of the solution becomes high and the via-filling material remaining on insulating film 102 becomes thick, necessitating extra steps of removing by polishing.

15       Next, the applied via-filling material 117 is solidified by pre-baking at 80 to 100°C for 90 to 180 seconds and baking at 180 to 230°C for 50 to 90 seconds to form via-filling body 107. Then, for example, an antireflection coating for ArF lithography (available from Clariant Japan KK) 108 is applied on this via-filling body 107 existing on and leveling off  
20 upper insulating film 102 by spin-coating and baked to form into a film (Fig. 1 (f)). The material of the antireflection coating is not limited to the above material and commercially available antireflection coatings can be used.

Thereafter, an ArF-excimer resist (available from Tokyo Oka  
25 Co., Ltd.) for example, was spin-coated on antireflection coating 108 and according to a usual photolithographic method, resist pattern 109 which serves as a mask when plasma etching is formed (Fig. 1 (g)). The

photosensitive resist used here is not limited to the above material and various resist materials including resists for g-ray, i-ray, KrF-excimer, F<sub>2</sub>-excimer, EB (electron beam), X-ray and E-UV (extreme-UV) can be used depending on the dimension of pattern to be formed.

5           In the next step, plasma etching is conducted with formed resist pattern 109 as an etching mask to create trench 110 in the upper part of upper insulating film 102 (Fig. 1 (h)). In plasma etching, the etching device used when etching usual SiOC film is employed and etching is conducted by using a gas containing a fluorine gas such as  
10   CF<sub>4</sub> as a main component under a pressure of 20 to 150 mTorr.

          In this embodiment, the polymer having a repeat unit represented by the formula (1) is used as via-filling material 117 in via hole 106 and thus when etching SiOC of upper insulating film 102, the etching rate of via-filling body 107 obtained from this via-filling material  
15   117 is the same or higher than that of upper insulating film 102. Therefore, in via-filling body 107, thickness reduction occurs at the same rate or faster than the reduction of upper insulating film 102. For these reasons, via-filling body 107 does not protrude from upper insulating film 102 in formed trench 110 and deposition from the  
20   decomposition in plasma or reaction products is not formed because via-filling body 107 is not protruded. In addition, downward etching of upper insulating film 102 is not prevented because there is no deposition and trench 110 can be formed well.

          Next, remaining resist pattern 109, anti-reflection coating  
25   108 and via-filling body 107 are removed and cleaned by O<sub>2</sub> plasma ashing and amine organic peeling solution to expose via hole 106 and upper wiring trench 111 in upper insulating film 102 (Fig. 1(i)).

By using a mixed etching gas of  $\text{CHF}_3$ ,  $\text{O}_2$  and inert gas Ar, stopper film 103 located at the bottom of via hole 106 is subjected to plasma etching with upper insulating film 102 as a mask and lower metal line 105 is exposed (Fig. 1 (j)).

5                Then after cleaning the surfaces of upper insulating film 102 and lower metal line 105 by using a remover of amine based organic solution, a copper film was formed by sputtering in via hole 106 and upper wiring trench 111. When necessary, a film of tantalum nitride can also be formed before forming copper sputtering layer in order to  
10 prevent copper from diffusing. Thereafter copper is further applied by plating to form second conductor 112 made of copper. This second conductor 112 comprises upper metal line 113 and inter-layer connection 114 and thus semiconductor integrated circuit 115 is completed (Fig. 1 (k)).

15                In the process for fabricating a semiconductor integrated circuit of this embodiment, the polymer having a repeat unit represented by the formula (1) is used as via-filling material 117 in via hole 106. Therefore, the via-filling body 107 obtained from via-filling material 117 does not protrude from upper insulating film 102 and deposition which  
20 is chemically stable and hard to decompose are not formed even if upper insulating film 102 and via-filling body 107 are etched simultaneously by plasma etching. Therefore, the flaw of deposition remaining in the opening part of via hole 106 after removing via-filling body 107 within via hole 106 does not occur. This eliminates the need for the extra steps of  
25 removing deposition chemically stable and hard to decompose which possibly causes a damage to interconnections in a semiconductor integrated circuit. Furthermore, upper metal line 113 can be formed

well when upper wiring trench 111 is filled with second conductor 112 made of copper and therefore disconnection due to faulty formation of upper metal line 113 can be prevented, making it possible to obtain a semiconductor integrated circuit with high reliability.

5                In this embodiment, anti-reflection coating 108 is formed on the via-filling body 107 formed when leveling upper insulating film 102 by filling via hole 106 with via-filling material 117. However, similar effect can be found and semiconductor integrated circuit with high reliability can also be obtained even by forming resist pattern 109  
10                directly on the film of via-filling body without applying this anti-reflection coating 108 and by etching upper insulating film 102 and via-filling body 107 together using this resist pattern 109 as a mask.

## EMBODIMENT 2

15                Fig. 2 is a cross-sectional view illustrating the steps of fabricating a semiconductor integrated circuit of Embodiment 2 using the via-filling material of the present invention, according to the via-first dual damascene process.

                 In Fig. 2, insulating film 202 is formed on semiconductor  
20                substrate 200 (Fig. 2 (a)) and resist pattern 201 is formed on this insulating film 202 (Fig. 2 (b)). Via hole 206 is created in insulating film 202 (Fig. 2 (c)), followed by removal of resist pattern 201 (Fig. 2 (d)). Thereafter via hole 206 is filled with via-filling material 217 (Fig. 2 (e)). The via-filling material 217 used here is the same as that used in  
25                Embodiment 1.

                 Next, resist pattern 209 is formed on the via-filling body 207 obtained by solidifying via-filling material 217 existing on and leveling

off insulating film 202 (Fig. 2 (f)), insulating film 202 and via-filling body 207 are subjected to plasma etching with this resist pattern 209 as an etching mask and trench 210 is created in the upper part of insulating film 202 (Fig. 2 (g)). Then remaining resist pattern 209 and via-filling body 207 are removed and cleaned to expose via hole 206 and wiring trench 211 (Fig. 2 (h)). Subsequently, via hole 206 and wiring trench 211 are filled with conductor of copper 212. This conductor 212 comprises metal line 213 and inter-layer connection 214 and thus semiconductor integrated circuit 215 is completed (Fig. 2 (i)).

The material and method employed in this embodiment are the same as those in Embodiment 1. The effect similar to that of Embodiment 1 is found and semiconductor integrated circuit with high reliability can be obtained.

### EMBODIMENT 3

This embodiment is carried out in the same manner as in Embodiment 1 except for using as via-filling material 117 a material comprising a copolymer of the first monomer represented by the formula (2):



wherein  $\text{R}_1$  is a member selected from the group consisting of hydrogen atom, fluorine atom, chlorine atom, bromine atom and methyl group;  $\text{R}_2$  is a member selected from the group consisting of hydrogen atom,  $\text{C}_{1-3}$

alkyl group and C<sub>1-4</sub> alkyl group in which the hydrogen atom is substituted by at least one kind of atoms of fluorine, chlorine and bromine atoms; and X is -C(=O)O- or -S(=O)<sub>2</sub>O-, and the second monomer which is an unsaturated compound containing an  
5 unsaturated group which brings about a copolymerization reaction with the first monomer and a functional group capable of crosslinking the copolymer.

In this embodiment, an unsaturated compound containing at least two unsaturated groups is particularly used as the second  
10 monomer.

Examples of the unsaturated compound containing at least two unsaturated groups are ester compounds obtained by condensing a carboxylic acid containing an unsaturated group or sulfonic acid containing an unsaturated group and alcohol containing an  
15 unsaturated group.

Concrete examples of the carboxylic acid containing an unsaturated group or sulfonic acid containing an unsaturated group are acrylic acid, methacrylic acid,  $\alpha$ -fluoroacrylic acid,  $\alpha$ -chloroacrylic acid,  $\alpha$ -bromoacrylic acid and vinyl sulfonic acid. Concrete examples of the  
20 alcohol containing an unsaturated group are vinyl alcohol, allyl alcohol, isopropenyl alcohol, propargyl alcohol, 1,1-dimethyl-2-propenyl alcohol and 1,1-dimethyl-2-propinyl alcohol.

The above copolymer is synthesized by polymerization reaction between the double bond in the first monomer and the  
25 unsaturated bond in the second monomer by heat or light. At this stage, at least one of the unsaturated groups existing in the unsaturated compound containing at least two unsaturated groups, which is the

second monomer, should remain in the copolymer.

In the above copolymer, when the number of the structural unit derived from the first monomer is assumed to be  $X_1$  and the number of the structural unit derived from the second monomer, i.e.,  
5 unsaturated compound, is assumed to be  $X_2$ , the composition ratio  $X_1/X_2$  is preferably in the range of 98/2 to 70/30.

In this embodiment, the copolymer used for the via-filling material contains at least 70 % of the structural unit derived from the first monomer and therefore, thickness reduction in via-filling body 107  
10 obtained from the via-filling material occurs at the same rate or faster than the reduction of upper insulating film 102 when upper insulating film 102 is etched in the preparation of semiconductor integrated circuit according to the dual damascene process shown in Fig. 1. For this reason, via-filling body 107 does not protrude from upper insulating film  
15 102 in formed trench 110 and deposition from the decomposition in plasma or reaction products is not formed. In addition, downward etching of upper insulating film 102 is not prevented because there is no deposition and thus trench 110 can be formed well.

In some cases, mixing of anti-reflection coating 108 and part  
20 of via-filling body 107 may occur in the step (f) of the process for preparing semiconductor integrated circuit shown in Fig. 1. It occurs when anti-reflection coating 108 is applied and heat-treated to form a film, particularly when heat-treating at a temperature of 180°C or higher in order to improve the anti-reflection property. However, in this  
25 embodiment, crosslinking reaction occurs in via-filling material 117 when via hole 106 is filled with via-filling material 117 and heating is conducted because the copolymer used for the via-filling material 117

contains at least 2 % of the structural unit derived from the second monomer which is an unsaturated compound containing at least two unsaturated groups and some of these unsaturated groups remain in the copolymer.

5                That is, in this embodiment, mixing of anti-reflection coating 108 and via-filling body 107 can be prevented even if the applied anti-reflection coating 108 is heat-treated at 180°C or higher, because the via-filling material 107 is in crosslinked state and therefore, decrease in dimensional accuracy of resist wiring pattern 109 caused by mixing of  
10 anti-reflection coating and via-filling body 107 can be prevented.

                 Accordingly, upper wiring trench 111 can be formed well, disconnection caused by faulty formation of upper metal line 113 can be prevented and semiconductor integrated circuit with high reliability can be prepared also by the process for preparing semiconductor integrated  
15 circuit using the via-filling material of this embodiment.

#### EMBODIMENT 4

                 This embodiment is carried out in the same manner as in Embodiment 3 except for using a copolymer in which the second  
20 monomer is unsaturated compound containing an unsaturated group and epoxy group as via-filling material 117.

                 Examples of the unsaturated compound containing an unsaturated group and epoxy group are esters of an acrylic acid selected from acrylic acid, methacrylic acid and  $\alpha$ -halo acrylic acid, and glycidyl  
25 alcohol.

                 In this embodiment, the copolymer also contains at least 70 % of the structural unit derived from the first monomer and therefore,



when upper insulating film 102 is etched in the preparation of semiconductor integrated circuit according to the dual damascene process, via-filling body 107 does not protrude from upper insulating film 102 in formed trench 110 and deposition from the decomposition in plasma or reaction products is not formed. Accordingly, downward etching of upper insulating film 102 is not prevented and thus trench 110 can be formed well.

In this embodiment, crosslinking reaction occurs in via-filling material 117 when via hole 106 is filled with via-filling material 117 and heat treatment is conducted because the copolymer used for the via-filling material 117 contains at least 2 % of the structural unit derived from the second monomer which is an unsaturated compound containing an unsaturated group and epoxy group and epoxy group is present in the copolymer.

That is, in this the embodiment, mixing of anti-reflection coating 108 and via-filling body 107 can be prevented even if the anti-reflection coating 108 is heat-treated at 180°C or higher and therefore, decrease in dimensional accuracy of resist pattern 109 caused by mixing of anti-reflection coating 108 and via-filling body 107 can be prevented.

Accordingly, upper wiring trench 111 can be formed well, disconnection caused by faulty formation of upper metal line 113 can be prevented and semiconductor integrated circuit with high reliability can be prepared also by the process for preparing semiconductor integrated circuit using the via-filling material of this embodiment.

#### EMBODIMENT 5

This embodiment is carried out in the same manner as in

Embodiment 3 except for using a mixture of the copolymer used in Embodiment 3 and an unsaturated compound containing at least two unsaturated groups as the via-filling material.

Examples of the unsaturated compound containing at least  
5 two unsaturated groups in this embodiment are ester compounds obtained by the reaction between a compound selected from multifunctional alcohols and multifunctional thiols such as ethylene glycol, diethylene glycol, triethylene glycol, propylene glycol, glycerin, pentaerythritol, mercapto ethanol, ethylene dithiol, and thiodiethanol  
10 and one organic acid containing an unsaturated group selected from acrylic acid, methacrylic acid,  $\alpha$ -fluoroacrylic acid,  $\alpha$ -chloroacrylic acid,  $\alpha$ -bromoacrylic acid and vinyl sulfonic acid.

In this embodiment, a catalyst which promote the reaction of unsaturated group may also be added to the mixture of the copolymer  
15 and the unsaturated compound containing at least unsaturated groups. Examples of the catalyst is azo nitrile compound such as 2,2'-azobisisobutyronitrile, azo amide compound such as 2,2'-azobis(N-butyl-2-methylpropion amide), alkyl azo compound such as azodi-tert-octane, and peroxide compound such as benzyl peroxide.

20 In this embodiment, the content of unsaturated compound containing at least two unsaturated groups in the via-filling material is preferably at most 25 % by weight. When the amount is more than 25 % by weight, the etching rate of via-filling body 107 becomes lower than the etching rate of upper insulating film 102.

25 Since the same copolymer that in Embodiment 3 is used in this embodiment, the effect similar to that of Embodiment 3 can be obtained. That is, trench 110 can be formed well when etching upper

insulating film 102 and the decrease of dimensional accuracy of resist pattern 109 is prevented by controlling the mixing of anti-reflection coating 108 and via-filling body 107.

In addition, this embodiment is free from the trouble of voids  
5 being generated by faulty filling even if via hole 106 having an aspect ratio of at least 4 or a pore size of at most  $0.15\text{ }\mu\text{m}$  is filled with via-filling material 117, because the unsaturated compound containing at least two unsaturated groups is mixed to the via-filling material 117 and the flowability of the via-filling material 117 is improved. Moreover, since  
10 the unsaturated compound mixed to the via-filling material 117 has at least two unsaturated groups, crosslinking reaction occurs by heat treatment conducted after the via-filling material 117 is filled in via hole 106 and then molecular weight increases infinitely. At the same time the unsaturated compound reacts with copolymer to create crosslinking,  
15 making it possible to prevent mixing of anti-reflection coating 108 and via-filling body 107.

Accordingly, upper wiring trench 111 can be formed well, disconnection caused by faulty formation of upper metal line 113 can be prevented and semiconductor integrated circuit with high reliability can  
20 be prepared also by the process for preparing semiconductor integrated circuit using the via-filling material of this embodiment.

#### EMBODIMENT 6

This embodiment is carried out in the same manner as in  
25 Embodiment 4 except for using a mixture of the copolymer used in Embodiment 4 and an epoxy compound containing at least two epoxy groups as the via-filling material.

Examples of the epoxy compound containing at least two epoxy groups is bisphenol A diglycidyl ether and trisphenol triglycidyl ether.

5 In this embodiment, the content of epoxy compound containing at least two epoxy groups in the via-filling material is preferably at most 25 % by weight. When the amount is more than 25 % by weight, the etching rate of via-filling body 107 becomes lower than the etching rate of upper insulating film 102.

In this embodiment, the same copolymer as in Embodiment 10 is used and therefore, the effect similar to that of Embodiment 4 can be obtained. That is, trench 110 can be formed well when etching upper insulating film 102 and the decrease of dimensional accuracy of resist wiring pattern 109 is prevented by controlling the mixing of anti-reflection coating 108 and via-filling body 107.

15 In addition, this embodiment is free from the trouble of voids being generated by faulty filling even if via hole 106 having an aspect ratio of at least 4 or a pore size of at most  $0.15\ \mu\text{m}$  is filled with via-filling material 117, because the epoxy compound containing at least two epoxy groups is mixed to the via-filling material 117, this epoxy 20 compound containing at least two epoxy groups is an oligomer having an average repeat number of at most 2 and because the flowability of the via-filling material 117 is improved. Moreover, since the epoxy compound mixed to the via-filling material 117 has at least two epoxy groups, crosslinking reaction occurs by heat treatment conducted after 25 the via-filling material 117 is filled in via hole 106 and then molecular weight increases infinitely. At the same time the epoxy compound reacts with copolymer to create crosslinking, making it possible to

prevent mixing of anti-reflection coating 108 and via-filling body 107.

Accordingly, upper wiring trench 111 can be formed well, disconnection caused by faulty formation of upper metal line 113 can be prevented and semiconductor integrated circuit with high reliability can be prepared also by the process for preparing semiconductor integrated circuit using the via-filling material of this embodiment.

### EMBODIMENT 7

This embodiment is carried out in the same manner as in Embodiment 3 except for using a via-filling material comprising a mixture obtained by mixing a compound selected from melamine compounds containing at least two methoxymethyl groups, urea compounds containing at least two methoxymethyl groups and epoxy compounds containing at least two epoxy groups to a copolymer of the first monomer and the second monomer which is an unsaturated compound having a functional group selected from hydroxyl group, carboxyl group and dicarboxylic anhydride group.

In this embodiment, examples of the unsaturated compound having a functional group selected from hydroxyl group, carboxyl group and dicarboxylic anhydride group are esters of an acrylic acid selected from acrylic acid, methacrylic acid and  $\alpha$ -halo acrylic acid, and ethylene glycol or propylene glycol; maleic acid; N-hydroxymaleimide and the like.

In this embodiment, examples of the melamine compound containing at least two methoxymethyl groups are hexakismethoxymethyl melamine and examples of urea compound containing at least two methoxymethyl groups are bismethoxymethyl ethylene urea. Examples of the epoxy compound containing at least

two epoxy groups are bisphenol A diglycidyl ether and trisphenol triglycidyl ether.

In this embodiment, the content of the compound mixed with the copolymer is at most 25 % by weight in the via-filling material.

5 When the amount is more than 25 % by weight, the etching rate of via-filling body 107 becomes lower than the etching rate of upper insulating film 102.

In this embodiment, the copolymer used in the via-filling material contains at least 70 % of the structural unit derived from the first monomer and therefore, when etching upper insulating film 102,  
10 trench 110 can be formed well.

Furthermore, this embodiment is free from the trouble of voids being generated by faulty filling even if via hole 106 having an aspect ratio of at least 4 or a pore size of at most 0.15  $\mu\text{m}$  is filled with  
15 via-filling material 117, because a compound selected from melamine compound containing at least two methoxymethyl groups, urea compound containing at least two methoxymethyl groups and epoxy compound containing at least two epoxy groups is mixed to the via-filling material 117 and the flowability of the via-filling material 117 is  
20 improved.

In addition, since the copolymer contains at least 2 % of the structural unit derived from the second monomer, any of the functional groups of hydroxyl group, carboxyl group and dicarboxylic anhydride group are present in the copolymer. Thus when via hole 106 is filled  
25 with via-filling material 117 and heat treated, these functional groups react with the compound selected from melamine compound containing at least two methoxymethyl groups, urea compound containing at least

two methoxymethyl groups and epoxy compound containing at least two epoxy groups to crosslink via-filling material 117.

That is, in this embodiment, mixing of anti-reflection coating 108 and via-filling body 107 can be prevented even if the applied anti-reflection coating 108 is heat-treated at 180°C or higher and therefore, decrease in dimensional accuracy of resist pattern 109 caused by mixing of anti-reflection coating 108 and via-filling body 107 can be prevented.

Accordingly, upper wiring trench 111 can be formed well, disconnection caused by faulty formation of upper metal line 113 can be prevented and semiconductor integrated circuit with high reliability can be prepared also by the process for preparing semiconductor integrated circuit using the via-filling material of this embodiment.

In the followings, the present invention is explained in more detail based on Examples.

15

#### EXAMPLE 1

The etching rate of widely used insulating film materials such as SiOC, SiO<sub>2</sub>, SiOF and SilK, was measured in the following manner.

Insulating film of SiOC, SiO<sub>2</sub> or SiOF was formed on a silicone wafer in a thickness of 1,000 nm by the CVD method. Also, insulating film of SilK spin-on-glass material was formed on a silicone wafer in a thickness of 1,000 nm by spin coating.

Each insulating film prepared in this way was subjected to plasma etching by using a mixed etching gas of C<sub>4</sub>F<sub>8</sub>/O<sub>2</sub>/Ar = 8/20/400 sccm under the condition of an RF power of 600 W and a pressure of 300 mTorr and etching rate was measured. The results are shown in Table 1.

Secondly, a film of via-filling body was formed by using the via-filling material of the present invention as described below.

A polymer in which the repeat unit is represented by the formula (1), the repeat number (n) of repeat unit is 50 and each group,  
5 i.e., X is  $-\text{C}(=\text{O})\text{O}-$ ,  $\text{R}_1$  is Cl and  $\text{R}_2$  is  $\text{CH}_3$ , was dissolved in a solvent to prepare a 7 % solution. This solution was applied to a silicon wafer by the spin coating method and baked and the via-filling body of 1,000 nm in thickness was formed.

The film of the via-filling body prepared in this way was  
10 subjected to plasma etching under the same condition as that in the case of the above insulating film, and etching rate was measured. The results are shown in Table 2.

#### EXAMPLES 2 to 15

15 The via-filling body was prepared by using the polymer having the same "n" and molecular structure as those in Example 1 except that each of X,  $\text{R}_1$  and  $\text{R}_2$  was as shown in the column Ex. 2 to 15 of Table 2. The film of the via-filling body was subjected to plasma etching under the same condition as that in the case of the above  
20 insulating film and the etching rate was measured. The results are shown in Table 2.

#### COMPARATIVE EXAMPLES 1 to 6

Polymethyl methacrylate (PMMA) resin, antireflection coating  
25 (DUV: available from Nissan Chemical Industries, Ltd. and AZ KrF-16: available from Clariant Japan KK), KrF resist (PEK-112: available from JSR Corporation), novolak resin and methoxymethylated



benzoguanamine which are conventional via-filling materials were respectively formed into a film of 1000 nm in thickness on a silicon wafer by spin coating. Each of these films was subjected to plasma etching under the same condition as that in the case of the above insulating film and the etching rate was measured. The results are shown in Table 3.

TABLE 1

Insulating film	Etching rate (nm/min)
SiOC	205
SiO <sub>2</sub>	134
SiOF	148
SilK (available from Dow-Chemical Co. Ltd.)	210

TABLE 2

	Group of via-filling material			Etching rate (nm/min)
	X	R <sub>1</sub>	R <sub>2</sub>	
Ex. 1	C(=O)O	Cl	CH <sub>3</sub>	213
Ex. 2	C(=O)O	Cl	C <sub>2</sub> H <sub>5</sub>	211
Ex. 3	C(=O)O	Cl	CH <sub>2</sub> CF <sub>3</sub>	253
Ex. 4	C(=O)O	Cl	CH <sub>2</sub> CCl <sub>3</sub>	342
Ex. 5	C(=O)O	Cl	CH <sub>2</sub> CBr <sub>3</sub>	357
Ex. 6	C(=O)O	Cl	C <sub>4</sub> F <sub>9</sub>	274
Ex. 7	C(=O)O	Cl	CH <sub>2</sub> CF <sub>2</sub> CF <sub>3</sub>	285
Ex. 8	C(=O)O	F	CH <sub>2</sub> CCl <sub>3</sub>	282
Ex. 9	C(=O)O	Br	CH <sub>2</sub> CCl <sub>3</sub>	354
Ex. 10	C(=O)O	CH <sub>3</sub>	CH <sub>2</sub> CCl <sub>3</sub>	236
Ex. 11	S(=O) <sub>2</sub> O	H	CH <sub>3</sub>	216
Ex. 12	S(=O) <sub>2</sub> O	H	C <sub>2</sub> H <sub>5</sub>	212
Ex. 13	S(=O) <sub>2</sub> O	H	CH <sub>2</sub> CF <sub>3</sub>	262
Ex. 14	S(=O) <sub>2</sub> O	H	CH <sub>2</sub> CCl <sub>3</sub>	330
Ex. 15	S(=O) <sub>2</sub> O	H	CH <sub>2</sub> CBr <sub>3</sub>	354

TABLE 3

	Conventional via-filling material	Etching rate (nm/min)
Com. Ex. 1	PMMA resin	125
Com. Ex. 2	DUV (available from Nissan Chemical Industries)	115
Com. Ex. 3	AZ KrF-16 (available from Clariant Japan KK)	102
Com. Ex. 4	KrF resist (PEK-112)	89
Com. Ex. 5	Novolak resin (i-ray resist)	65
Com. Ex. 6	Methoxymethylated benzoguanamine	115

From comparison of Tables 1 to 3, the etching rate of the via-filling body obtained from the via-filling material of the present invention was found to be higher than etching rate of the insulating film used in the dual damascene process and the etching rate of the conventional via-filling material was found to be lower than the etching rate of the above insulating film.

The via-filling material of the present invention has the effect that the via-filling material does not protrude from the insulating film even when etched at the same time as the insulating film.

10

#### EXAMPLES 16 to 30

First, the etching rate of insulating film material SiOC, SiO<sub>2</sub>, SiOF and SilK which are widely used was measured in the following manner.

15 Insulating film of each of SiOC, SiO<sub>2</sub> and SiOF was formed on a silicon wafer in a thickness of 1,000 nm by the CVD method. Also, insulating film of SilK spin-on-glass material was formed on a silicon wafer in a thickness of 1,000 nm by spin coating.

Each insulating film formed in this way was subjected to plasma etching using mixed etching gas CHF<sub>3</sub>/CF<sub>4</sub>/O<sub>2</sub>/Ar = 50/25/15/300 sccm, under conditions of an RF power of 400 W and pressure of 45 mTorr and the etching rate was measured. The results are shown in Table 4.

25 Next, a film of 1000 nm in thickness was formed on a silicon wafer in the same manner as in Examples 1 to 15 using the via-filling material used in Examples 1 to 15. The film of the via-filling body obtained from the via-filling material was subjected to plasma etching

using mixed etching gas of  $\text{CHF}_3/\text{CF}_4/\text{O}_2/\text{Ar} = 50/25/15/300$  sccm under conditions of an RF power of 400 W and a pressure of 45 mTorr and the etching rate was measured. The results are shown in Table 5.

5

COMPARATIVE EXAMPLES 7 to 12

A film of 1,000 nm in thickness was formed on a silicon wafer in the same manner as in Comparative Examples 1 to 6 using the conventional via-filling material used in Comparative Examples 1 to 6. This film of the via-filling body was subjected to plasma etching using  
10 mixed etching gas of  $\text{CHF}_3/\text{CF}_4/\text{O}_2/\text{Ar} = 50/25/15/300$  sccm under conditions of an RF power of 400 W and a pressure of 45 mTorr and the etching rate was measured. The results are shown in Table 6.

TABLE 4

Insulating film	Etching rate (nm/min)
SiOC	340
SiO <sub>2</sub>	218
SiOF	251
SilK (available from Dow-Chemical Co. Ltd.)	345

TABLE 5

	Group of via-filling material			Etching rate (nm/min)
	X	R <sub>1</sub>	R <sub>2</sub>	
Ex. 16	C(=O)O	Cl	CH <sub>3</sub>	355
Ex. 17	C(=O)O	Cl	C <sub>2</sub> H <sub>5</sub>	348
Ex. 18	C(=O)O	Cl	CH <sub>2</sub> CF <sub>3</sub>	422
Ex. 19	C(=O)O	Cl	CH <sub>2</sub> CCl <sub>3</sub>	570
Ex. 20	C(=O)O	Cl	CH <sub>2</sub> CBr <sub>3</sub>	595
Ex. 21	C(=O)O	Cl	C <sub>4</sub> F <sub>9</sub>	450
Ex. 22	C(=O)O	Cl	CH <sub>2</sub> CF <sub>2</sub> CF <sub>3</sub>	460
Ex. 23	C(=O)O	F	CH <sub>2</sub> CCl <sub>3</sub>	480
Ex. 24	C(=O)O	Br	CH <sub>2</sub> CCl <sub>3</sub>	580
Ex. 25	C(=O)O	CH <sub>3</sub>	CH <sub>2</sub> CCl <sub>3</sub>	400
Ex. 26	S(=O) <sub>2</sub> O	H	CH <sub>3</sub>	360
Ex. 27	S(=O) <sub>2</sub> O	H	C <sub>2</sub> H <sub>5</sub>	350
Ex. 28	S(=O) <sub>2</sub> O	H	CH <sub>2</sub> CF <sub>3</sub>	438
Ex. 29	S(=O) <sub>2</sub> O	H	CH <sub>2</sub> CCl <sub>3</sub>	550
Ex. 30	S(=O) <sub>2</sub> O	H	CH <sub>2</sub> CBr <sub>3</sub>	590

TABLE 6

	Conventional via-filling material	Etching rate (nm/min)
Com. Ex. 7	PMMA resin	174
Com. Ex. 8	DUV (available from Nissan Chemical Industries)	142
Com. Ex. 9	AZ KrF-16 (available from Clariant Japan KK)	140
Com. Ex. 10	KrF resist (PEK-112)	138
Com. Ex. 11	Novolak resin (i-ray resist)	105
Com. Ex. 12	Methoxymethylated benzoguanamine	142

From comparison of Tables 4 to 6, the etching rate of the via-filling body obtained from the via-filling material of the present invention was found to be higher than etching rate of the insulating film used in the dual damascene process and the etching rate of the via-filling body obtained from the conventional via-filling material was found to be lower than the etching rate of the above insulating film.

The via-filling material of the present invention has the effect that the via-filling material does not protrude from the insulating film even when etched at the same time as the insulating film.

10

### EXAMPLE 31

A semiconductor integrated circuit was fabricated using the via-filling material of the present invention by the dual damascene method and the generation of deposition after etching was examined.

15           The process for fabricating the semiconductor integrated circuit of this Example is described referring to Fig. 1.

First, lower insulating film 104 of SiOC of 800 nm in thickness was formed on semiconductor substrate 100 by the CVD (Chemical Vapor Deposition) method and a wiring trench was formed by a common photolithographic method. After a copper seed layer was formed by sputtering, by forming the first conductor by a copper plating process and further leveling by the CMP (Chemical Mechanical Polishing) method, a structure in which lower metal line 105 made from copper was embedded into lower insulating layer 104 was prepared.

20           Also, etching stopper film 103 made of SiN was formed in a thickness of 60 nm by sputtering and upper insulating layer 102 was formed by the CVD method and leveled by the CMP method so that the thickness of

insulating layer 102 became 1000 nm (Fig. 1 (a)).

Next, resist pattern 101 was formed using a common photolithographic method (Fig. 1 (b)), via hole 106 was formed by etching (Fig. 1 (c)) and the resist pattern was removed (Fig. 1 (d)).

5           Then, the 7 % polymer solution described in Example 1 which is the via-filling material of the present invention was applied by spin coating to fill via hole 106 with via-filling material 117 and upper insulating film 102 was leveled (Fig. 1 (e)).

          The via-filling material 117 which was filled was solidified by  
10 pre-baking at 150°C for 60 seconds and baking at 220°C for 60 seconds and via-filling body 107 was formed. On this via-filling body 107, organic antireflection coating material (AZ-ArF: available from Clariant Japan KK) was applied by spin coating and antireflection coating 108 was formed by heating at 100°C for 60 seconds (Fig. 1 (f)). Resist  
15 material for ArF excimer laser (available from Tokyo Ohka Kogyo Co., Ltd) was applied and by processing with the usual photolithographic method, resist pattern 109 was formed (Fig. 1 (g)).

          Next, upper insulating film 102 and via-filling body 107 were subjected to plasma etching at the same time using etching gas of  
20  $C_4F_8/O_2/Ar = 8/20/400$  sccm under the conditions of an RF power of 600 W and pressure of 30 mTorr and trench 110 of a depth of 600 nm was formed (Fig. 1 (h)).

          Then, resist pattern 109, antireflection coating 108 and via-filling body 107 remaining in the via hole were removed by an  $O_2$  plasma  
25 ashing and amine type organic solvent and etching stopper film 103 made of SiN was exposed (Fig. 1 (i)). At this point, via hole 106 was observed to find whether deposition due to etching had developed or not.

In this Example, deposition had not developed and the via-filling material of the present invention was found to be particularly effective for preventing development of deposition in the etching step when preparing a semiconductor integrated circuit according to the dual  
5 damascene method.

The etching stopper film was then removed (Fig. 1 (j)), copper was precipitated to via hole 106 and wiring trench 111 by copper sputtering and copper plating. Leveling was conducted by the CMP method to form upper metal line 113 and inter-layer connection 114 and  
10 semiconductor integrated circuit 115 was formed (Fig. 1 (k)).

In the process for preparing the semiconductor integrated circuit of this Example, deposition did not develop in the opening part of the via hole and so faulty formation of the upper metal line did not occur. As a result, disconnection is prevented and a semiconductor integrated  
15 circuit with high reliability can be obtained.

#### EXAMPLES 32 to 45

A semiconductor integrated circuit was fabricated in the same manner as in Example 31 except that the via-filling material of the  
20 polymer described in Examples 2 to 15 was used instead of the via-filling material used in Example 31. After the step of Fig. 1 (i), via hole 106 was observed to find whether deposition due to etching had developed or not.

In all of examples 32 to 45, deposition had not developed and  
25 the via-filling material of the present invention was found to be particularly effective for preventing development of deposition in the etching step when preparing a semiconductor integrated circuit



according to the dual damascene method.

In the process for preparing the semiconductor integrated circuit of Examples 32 to 45, deposition did not develop in the opening part of the via hole and so faulty formation of the upper metal line did not occur. As a result, disconnection is prevented and a semiconductor integrated circuit with high reliability can be obtained.

#### COMPARATIVE EXAMPLES 13 to 18

A semiconductor integrated circuit was fabricated in the same manner as in Example 31 except that the conventional via-filling material described in Comparative Examples 1 to 6 was used instead of the via-filling material used in Example 31. After the step of Fig. 1 (i), via hole 106 was observed to find whether deposition due to etching had developed or not.

Development of deposition was found in all of Comparative Examples 13 to 18. In other words, in the semiconductor integrated circuit prepared using the conventional via-filling material described in Comparative Examples 1 to 6, faulty formation of the upper metal line occurred and the semiconductor integrated circuit was not excellent in reliability.

#### EXAMPLE 46

A semiconductor integrated circuit was fabricated in the same manner as in Example 31 except that plasma etching was conducted using mixed etching gas of  $\text{CHF}_3/\text{CF}_4/\text{O}_2/\text{Ar} = 50/25/15/300$  sccm under the conditions of an RF power of 400 W and pressure of 45 mTorr in plasma etching in the step of Fig. 1 (h) of

Example 31. After the step of Fig. 1 (i), via hole 106 was observed to find whether deposition due to etching had developed or not.

In the present Example, deposition did not develop. That is, the via-filling material of the present invention was found to be particularly effective for preventing development of deposition in the etching step when preparing a semiconductor integrated circuit according to the dual damascene method.

In the process for preparing the semiconductor integrated circuit of the present Example, deposition did not develop in the opening part of the via hole and so faulty formation of the upper metal line did not occur. As a result, disconnection is prevented and a semiconductor integrated circuit with high reliability can be obtained.

#### EXAMPLES 47 to 60

A semiconductor integrated circuit was fabricated in the same manner as in Example 46 except that the via-filling material of the polymer described in Examples 2 to 15 was used instead of the via-filling material used in Example 46. After the step of Fig. 1 (i), via hole 106 was observed to find whether deposition due to etching had developed or not.

In all of Examples 47 to 60, deposition had not developed and the via-filling material of the present invention was found to be particularly effective for preventing development of deposition in the etching step when preparing a semiconductor integrated circuit according to the dual damascene method.

In the process for preparing the semiconductor integrated circuit of Examples 47 to 60, deposition did not develop in the opening

part of the via hole and so faulty formation of the upper metal line did not occur. As a result, disconnection is prevented and a semiconductor integrated circuit with high reliability can be obtained.

5

#### COMPARATIVE EXAMPLES 19 to 24

A semiconductor integrated circuit was fabricated in the same manner as in Example 46 except that the conventional via-filling material described in Comparative Examples 1 to 6 was used instead of the via-filling material used in Example 46. After the step of Fig. 1 (i),  
10 via hole 106 was observed to find whether deposition due to etching had developed or not.

Development of deposition was found in all of Comparative Examples 19 to 24. In other words, in the semiconductor integrated circuit prepared using the conventional via-filling material described in  
15 Comparative Examples 1 to 6, faulty formation of the upper metal line occurred and the semiconductor integrated circuit was not excellent in reliability.

#### EXAMPLE 61

20 The monomer represented by the above formula (2), in which X was  $-\text{C}(=\text{O})\text{O}-$ ,  $\text{R}_1$  was  $\text{C1}$  and  $\text{R}_2$  was  $\text{CH}_2\text{CCl}_3$ , was used as the first monomer and allylester  $\alpha$ -chloroacrylate was used as the second monomer. The two monomers were mixed and thermally polymerized by agitating at  $150^\circ\text{C}$  for 10 hours. A copolymer with a composition  
25 ratio of  $\text{X}_1/\text{X}_2 = 80/20$ , that is copolymer 1 of Table 7, was obtained.

Using this copolymer 1, the via-filling material was prepared in the same manner as in Example 1 and applied to a silicon wafer.

Then, a via-filling body of a thickness of 1,000 nm was formed by pre-baking at 150°C for 60 seconds and baking at 220°C for 60 seconds and sample A for measuring etching rate was prepared. Sample A which is the via-filling body film was subjected to plasma etching under the same  
5 conditions as in Example 1 and the etching rate was measured. The results are shown in Table 8 along with the compounding of the via-filling material except for the solvent.

On this via-filling body formed on the silicon wafer, organic antireflection coating material (ArF-1C1B: available from Clariant Japan  
10 KK) was applied by spin coating and an antireflection coating was formed by heating at 200°C for 60 seconds to prepare sample B.

The silicon wafer of sample B was cut and the section was observed by a scanning electron microscope. Then, development of mixing was determined by whether a boundary existed between the  
15 via-filling body and the antireflection film. The results are shown in Table 8. Mixing was determined to have occurred, if the boundary has been lost in this observation.

#### EXAMPLES 62 to 65

20 The via-filling material was prepared in the same manner as in Example 61 except for respectively using copolymer 2, copolymer 3, copolymer 6 and copolymer 8 of which the first monomer, second monomer and composition ratio of the structural unit derived therefrom are as described in Table 7. Furthermore, sample A and sample B were  
25 prepared using this via-filling material and the etching rate of the via-filling body and development of mixing were evaluated in the same manner as in Example 61. The results are shown in Table 8 along with

the compounding of the via-filling material except for the solvent.

EXAMPLES 66 and 67

The via-filling material was prepared in the same manner as  
5 in Example 61 except for respectively using copolymer 9 in which the  
composition ratio of the structural unit derived from the first monomer  
is 68 % and copolymer 10 in which the composition ratio of the  
structural unit derived from the second monomer is 1.5 %, both of which  
are shown in Table 7 and have the same first monomer and the second  
10 monomer as in the copolymer used in Example 61. Furthermore,  
sample A and sample B were prepared using this via-filling material and  
the etching rate of the via-filling body and development of mixing were  
evaluated in the same manner as in Example 61. The results are  
shown in Table 8 along with the compounding of the via-filling material  
15 except for the solvent.

TABLE 7

	First monomer			Second monomer	$X_1/X_2$
	X	R <sub>1</sub>	R <sub>2</sub>		
Copolymer 1	C(=O)O	Cl	CH <sub>2</sub> CCl <sub>3</sub>	Allylester $\alpha$ -chloroacrylate	80/20
Copolymer 2	C(=O)O	Cl	CH <sub>2</sub> CCl <sub>3</sub>	Allylester $\alpha$ -chloroacrylate	98/2
Copolymer 3	C(=O)O	Cl	CH <sub>2</sub> CCl <sub>3</sub>	Allylester $\alpha$ -chloroacrylate	70/30
Copolymer 4	C(=O)O	Cl	CH <sub>2</sub> CCl <sub>3</sub>	Allylester $\alpha$ -chloroacrylate	90/10
Copolymer 5	C(=O)O	Cl	CH <sub>2</sub> CCl <sub>3</sub>	$\alpha$ -chloroacrylate	80/20
Copolymer 6	C(=O)O	Cl	CH <sub>2</sub> CCl <sub>3</sub>	Glycidylester $\alpha$ -chloroacrylate	80/20
Copolymer 7	C(=O)O	Cl	CH <sub>2</sub> CF <sub>3</sub>	Ethylene glycol monoacrylate	80/20
Copolymer 8	S(=O) <sub>2</sub> O	H	CH <sub>2</sub> CF <sub>3</sub>	Isopropenyl $\alpha$ -chloroacrylate	80/20
Copolymer 9	C(=O)O	Cl	CH <sub>2</sub> CCl <sub>3</sub>	Allylester $\alpha$ -chloroacrylate	68/32
Copolymer 10	C(=O)O	Cl	CH <sub>2</sub> CCl <sub>3</sub>	Allylester $\alpha$ -chloroacrylate	98.5/1.5

$X_1/X_2$  represents the composition ratio of copolymer

**TABLE 8**

	Via-filling material	Etching rate (nm/min)	Development of mixing
Ex. 61	Copolymer 1	248	None
Ex. 62	Copolymer 2	325	None
Ex. 63	Copolymer 3	233	None
Ex. 64	Copolymer 6	238	None
Ex. 65	Copolymer 8	245	None
Ex. 66	Copolymer 9	200	None
Ex. 67	Copolymer 10	335	Mixed

As obvious from the results of Examples 61 to 67, the etching rate of a via-filling body, obtained from a via-filling material using a copolymer in which the composition ratio of the structural unit derived from the first monomer represented by the above formula (2) is 98 to 70 %, was larger than the etching rate of the upper insulating film. In addition, a via-filling material, using a copolymer in which the composition ratio of the structural unit derived from the second monomer, which is an unsaturated compound having at least two unsaturated groups or a unsaturated compound having an epoxy group is at least 2 %, formed a via-filling body in which mixing with the antireflection coating did not occur, even when an antireflection coating was applied and heated at a temperature of 180°C or higher.

15

**EXAMPLES 68 to 73**

Sample A and sample B were prepared in the same manner as in Example 61 except that the via-filling material shown in Table 9 was used and regarding the via-filling body obtained from the via-filling

materials, the etching rate and development of mixing were evaluated. The results are shown in Table 9 along with the compounding of the via-filling material except for the solvent.

5

#### EXAMPLE 74

Sample A and sample B were prepared in the same manner as in Example 61 except that a via-filling material, in which the ratio of the compound added and mixed to the copolymer was greater than 25 % by weight in the above mixture, was used. Regarding the via-filling  
10 body obtained from the via-filling material, the etching rate and development of mixing were evaluated. The results are shown in Table 9 along with the compounding of the via-filling material except for the solvent.



TABLE 2

	Copolymer (Cp)	Via-filling material		Etching rate (nm/min)	Development of mixing
		Compound added (Cm)	Composition ratio (Cp/Cm)		
Ex. 68	Copolymer 4	Ethylene glycol diacrylate	75/25	251	None
Ex. 69	Copolymer 4	Ethylene glycol diacrylate	95/5	268	None
Ex. 70	Copolymer 5	Dimethoxymethylene urea	75/25	221	None
Ex. 71	Copolymer 6	Bisphenol A diglycidyl ether	75/25	212	None
Ex. 72	Copolymer 7	Hexakis(methoxymethyl) melamine	75/25	220	None
Ex. 73	Copolymer 8	Glycerin triacrylate	75/25	229	None
Ex. 74	Copolymer 4	Ethylene glycol diacrylate	74/26	202	None

Cp/Cm represents the weight ratio of Copolymer Cp and Compound Cm added

As obvious from the results of Examples 68 to 74, when the via-filling material was a mixture obtained by adding a compound that reacts with a functional group of the second monomer capable of crosslinking the copolymer to a copolymer of a first monomer represented by the above formula (2) and a second monomer having an unsaturated group and a functional group capable of crosslinking the obtained copolymer, has a composition ratio of 98 to 70 % of the structural unit derived from the first monomer of the copolymer and contains at most 25 % by weight of the above compound, the etching rate of the via-filling body obtained from this via-filling material was larger than the etching rate of the upper insulating layer. Furthermore, in the via-filling body obtained from this via-filling material, mixing with the antireflection coating did not occur, even when an antireflection coating was applied and heated at a temperature of 180°C or higher.

15

#### EXAMPLES 75 to 85

A semiconductor integrated circuit was fabricated in the same manner as in Example 31 except that the via-filling material described in Examples 61 to 65 and 68 to 73 was used instead of the via-filling material used in Example 31 and antireflection coating was formed by applying organic antireflection coating material (ArF-1C1B: available from Clariant Japan KK) by spin coating and heating at 200°C for 60 seconds. After the step of Fig. 1 (i), via hole 106 was observed to find whether deposition due to etching had developed or not.

25

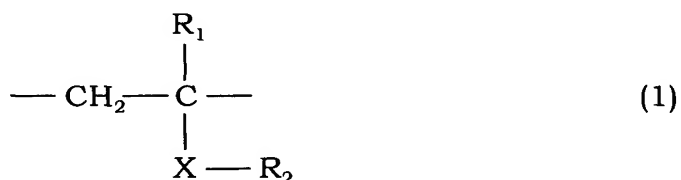
In all of examples 75 to 85, deposition had not developed and the via-filling material of the present invention was found to be particularly effective for preventing development of deposition in the

etching step when preparing a semiconductor integrated circuit according to the dual damascene method. Also, according to the via-filling material of the present invention, even when heating the antireflection coating at 180°C or higher, mixing did not develop between antireflection coating 108 and via-filling body 107 and an accurate resist pattern 109 was formed.

In the process for preparing the semiconductor integrated circuit of Examples 75 to 85, because a via hole opening part with excellent dimensional accuracy was formed and deposition did not develop in the opening part of the via hole, faulty formation of the upper metal line did not occur. As a result, disconnection is prevented and a semiconductor integrated circuit with high reliability can be obtained.

#### INDUSTRIAL APPLICABILITY

The via-filling material of the present invention comprises as the repeat unit a polymer represented by the following formula (1).



wherein R<sub>1</sub> is a member selected from the group consisting of hydrogen atom, fluorine atom, chlorine atom, bromine atom and methyl group; R<sub>2</sub> is a member selected from the group consisting of hydrogen atom, C<sub>1-3</sub> alkyl group and C<sub>1-4</sub> alkyl group in which the hydrogen atom is substituted by at least one kind of atoms of fluorine, chlorine and bromine atom; and X is -C(=O)O- or -S(=O)<sub>2</sub>O-. According to this, the

via-filling material of the present invention has the effect of preventing the development of chemically stable and hard to remove deposition which forms around the protrusion of the via-filling body, as the via-filling body does not protrude from the insulating film, even when the  
5 via-filling body obtained by solidifying the above via-filling material and the insulating film are etched at the same time.

Also, the via-filling material of the present invention comprises a copolymer of a first monomer represented by the following formula (2):

10



15 wherein  $\text{R}_1$  is a member selected from the group consisting of hydrogen atom, fluorine atom, chlorine atom, bromine atom and methyl group;  $\text{R}_2$  is a member selected from the group consisting of hydrogen atom,  $\text{C}_{1-3}$  alkyl group and  $\text{C}_{1-4}$  alkyl group in which the hydrogen atom is substituted by at least one kind of atoms of fluorine, chlorine and  
20 bromine atoms; and X is  $-\text{C}(=\text{O})\text{O}-$  or  $-\text{S}(=\text{O})_2\text{O}-$ ,

and a second monomer which contains an unsaturated group which brings about a copolymerization reaction with the first monomer and a functional group capable of crosslinking the obtained copolymer. According to this, development of chemically stable and hard to remove  
25 deposition which forms around the protrusion of the via-filling body, can be prevented as the via-filling body does not protrude from the insulating film, even when the via-filling body obtained by solidifying the

above via-filling material and the insulating film are etched at the same time. Furthermore, mixing of the antireflection coating and the via-filling body can be prevented, even when the antireflection coating applied on the via-filling body is heated at a temperature of at least  
5 180°C and a decrease in dimensional accuracy of the resist pattern caused by mixing of the antireflection coating with the via-filling body can be prevented.

In the process for preparing the semiconductor integrated circuit of the present invention, as the via-filling material to be filled in  
10 the via hole, a via-filling material, which comprises a polymer containing a repeat unit represented by the above formula (1) or a copolymer of a first monomer represented by the above formula (2) and a second monomer having a unsaturated group which brings about a copolymerization reaction with the first monomer and a functional group  
15 capable of crosslinking the obtained copolymer, is used. Therefore, even when the insulating film and the via-filling body obtained by solidifying the via-filling material are etched at the same time, the via-filling body does not protrude from the insulating film and deposition does not pile up, so a favorable trench can be formed, without etching  
20 downward into the insulating film being inhibited.

Also, the disadvantage of deposition remaining around the opening part of the via hole does not occur so the extra step of removing this chemically stable and hard to decompose deposition which may damage the wiring of the semiconductor integrated circuit becomes  
25 unnecessary. Furthermore, when a wiring trench is filled with a copper conductor, good metal line can be obtained and as a result, disconnection due to faulty formation of metal line is prevented and a

semiconductor integrated circuit with high reliability can be obtained.